

Surface Seals Reduce 1,3-Dichloropropene and Chloropicrin Emissions in Field Tests

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ABSTRACT

Reducing emissions is essential for minimizing the impact of soil fumigation on the environment. Water application to the soil surface (or water seal) has been demonstrated to reduce 1,3-dichloropropene (1,3-D) emissions in soil column tests. This study determined the effectiveness of water application to reduce emissions of 1,3-D and chloropicrin (CP) in comparison to other surface seals under field conditions. In a small-plot field trial on a Hanford sandy loam soil (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) in the San Joaquin Valley, CA, Telone C35 (61% 1,3-D and 35% CP) was shank-applied at a depth of 46 cm at a rate of 610 kg ha⁻¹. Soil surface seal treatments included control (no tarp and no water application), standard high density polyethylene (HDPE) tarp over dry and pre-irrigated soil, virtually impermeable film (VIF) tarp, initial water application by sprinklers immediately following fumigation, and intermittent water applications after fumigation. The atmospheric emissions and gas-phase distribution of fumigants in soil profile were monitored for 9 d. Among the surface seals, VIF and HDPE tarp over dry soil resulted in the lowest and the highest total emission losses, respectively. Intermittent water applications reduced 1,3-D and CP emissions significantly more than HDPE tarp alone. The initial water application also reduced emission peak and delayed emission time. Pre-irrigated soil plus HDPE tarp reduced fumigant emissions similarly as the intermittent water applications and also yielded the highest surface soil temperature, which may improve overall soil pest control.

SOIL FUMIGATION is used to control a variety of nematode, disease, and weed pests in agriculture. In 2003, 15 million kilograms of soil fumigants were applied to 90 000 ha in California (California Department of Pesticide Regulation, 2003; Trout, 2005). Soil fumigants are heavily regulated due to toxic properties and environmental impacts of gaseous emissions. One of the most widely used and effective soil fumigants, methyl bromide (MeBr), is being phased out of use because of its destruction of stratospheric ozone (Honaganahalli and Seiber, 1997), which absorbs UV radiation from the sun and reduces harm to people and terrestrial and aquatic ecosystems on the ground (Casanova, 2002). Some alternative fumigant products such as Telone II (1,3-dichloropropene or 1,3-D), or Telone C35 [combination of 1,3-D and chloropicrin (CP)] have been registered and used increasingly in recent years (Trout, 2005). Some of the alternative fumigants to MeBr are volatile organic compounds (VOCs) that can react with oxides

of nitrogen in the presence of sunlight and form harmful ground level ozone (Segawa, 2005). While soil fumigation is currently heavily regulated, even more stringent regulations are likely being considered. Minimizing emissions is critical to maintaining practical use of alternative fumigants for production of high value crops, protecting workers and bystanders during fumigation, and minimizing the detrimental impact on the environment.

Soil surface barriers with plastic tarps, such as standard high density polyethylene (HDPE), are commonly used to control fumigant emissions. The HDPE, however, does not effectively reduce 1,3-D emissions because of high permeability to this compound (Wang et al., 1999; Papiernik and Yates, 2002). The HDPE tarp is expensive (about \$2000 ha⁻¹ over shank broadcast applications in California for purchase, placement, removal, and disposal of the tarp). Another potentially effective tarp to reduce emissions is virtually impermeable film (VIF), which has much lower permeability to most fumigants than HDPE (Wang et al., 1999; Noling, 2002a; Thomas et al., 2004, 2006). Virtually impermeable film, however, costs substantially more than HDPE. Anecdotal reports indicate that maintaining the low permeability property of the film in large field applications may be difficult due to stretching and inadequate materials for gluing sheets together.

Some studies showed that high water content in surface soil provided a more effective barrier to 1,3-D movement than HDPE tarp (Gan et al., 1998; Thomas et al., 2003). Laboratory column and small field plot tests showed that water applications to the soil surface in combination with HDPE tarp greatly reduced MeBr emissions (Jin and Jury, 1995; Wang et al., 1997). Water seals, especially with intermittent applications after shank injection, showed promising results to reduce methyl isothiocyanate (MITC) emissions from applications of metam-sodium (MITC generator) although mixed results were obtained from intermittent water caps over sprinkler chemigation in field studies (Sullivan et al., 2004).

We tested the potential of using water application to the soil surface to reduce 1,3-D emissions from soil columns (Gao and Trout, 2006). The results showed that spraying water on the soil surface can reduce 1,3-D emissions more effectively than HDPE tarp. Water seals reduced peak emissions more effectively than cumulative emissions, mainly due to the abrupt reduction of emission rate after each water application. Initial water application immediately after fumigant injection reduced peak emissions and delayed the emission peak time, which is important to protect workers and bystanders during fumigation. Water application to the soil surface or water seal (costs of \$100 to \$700 ha⁻¹) is more economical than plastic tarps in field applications.

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The objective of this study was to determine if water applications to the soil surface can effectively reduce emissions of 1,3-D and CP from shank application of Telone C35 under field conditions. Water application treatments were compared to plastic tarps (HDPE and VIF) and the combination of water application and HDPE tarp.

MATERIALS AND METHODS

Chemicals and Plastic Materials

All organic chemicals used in the laboratory analysis were pesticide grade. Cis- and trans-1,3-D (purity of 98.9%) were provided by Dow AgroSciences (Indianapolis, IN). Chloropicrin (purity of 99.9%) was provided by Niklor Chemical Company (Mojave, CA). Sodium sulfate anhydrous (Na_2SO_4 , 10–60 mesh, ACS grade) was obtained from Fisher Scientific (Tustin, CA). Standard (1-mil or 0.025-mm thickness) HDPE film (Tyco Plastics, Princeton, NJ) and Bromostop VIF (1-mil thickness, Bruno Rimini Corp, London, UK) were provided by TriCal (Hollister, CA). Telone C35 (61% 1,3-D; 35% CP; and 4% inert ingredients) for field applications was provided by Dow AgroSciences (Indianapolis, IN).

Field Trial and Treatment

A field trial with small plots (9×3 or 9×9 m depending on treatment) was conducted in summer 2005, at the USDA-ARS San Joaquin Valley Agricultural Science Center, Parlier, CA ($36^\circ 35' 36.74''$ N; $119^\circ 30' 48.71''$ W). The soil is a Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents). The selected soil properties are reported in Table 1. The soil was cultivated to 75-cm depth before fumigation. The soil surface was dry (30 g kg^{-1} or 3% water content) before treatments were applied. A dry soil surface is typical for fall fumigations before orchard or vineyard planting. About 13 mm of water was sprinkled onto the field 1 wk before the field trial and the surface was disked to break down large soil clods. During the field trial, the maximum and minimum air temperature ranged from 37 to 41°C and 21 to 24°C , respectively.

Telone C35 was applied on 13 July by shank injection to a depth of 46 cm with a spacing between shanks of 46 cm at a rate of 610 kg ha^{-1} (the maximum allowable rate in California, 332 lb ac^{-1} AI [active ingredient] 1,3-D) by a commercial applicator (TriCal, Hollister, CA). Application began at 0830 h and was completed within 30 min. A rectangular area (150 m long \times 9 m wide) was fumigated in two passes using standard Telone application equipment. The fumigant tank was weighed before and after each pass to determine the actual amount of fumigant applied. The target rate was achieved. Immediately following the Telone C35 application, the soil surface was disked and harrowed to disrupt any shank traces and create a

smooth surface. Following disking, the appropriate tarp or water treatments were applied. Treatments were: (i) control (dry soil without tarp or water applications), (ii) HDPE tarp over dry soil, (iii) VIF tarp over dry soil, (iv) pre-irrigated soil plus HDPE tarp (56 mm water was sprinkled on the surface 48 h before fumigation; this amount of water wet the soil to 30-cm depth to its field capacity), (v) initial water application immediately following fumigation (19 mm water was sprinkled on the dry soil surface), and (vi) intermittent water applications (initial 19 mm water sprinkled immediately following fumigation plus 4.2 mm water sprinkled on soil surface at first sunset [8 h], first sunrise [22 h], noon [28 h], second sunset [32 h], and second sunrise [48 h] following fumigation).

Individual plots were 9×9 m for water application treatments and 9×3 m for the control and tarped treatments. Tarps with a width of 3.7 m were placed on the fumigated soil immediately after postfumigation tillage using a standard fumigation rig with the shanks removed. Tarp application was by a single pass perpendicular to the fumigation direction (across the plots) and tarp edges were inserted 20 cm deep into the soil. Sprinkler water was applied to each plot with four Hunter PGP rotary sprinklers set for quarter circle application placed in the corners of each plot (9-m spacing, 8.5 mm h^{-1} application rate). Each rotary sprinkler was adjusted depending on wind direction changes to achieve uniform water application into each plot. Water applied to the plots was measured by water meters. The 19 mm of water in the initial applications was sufficient to wet the soil to near field capacity to a 10-cm depth. The intermittent 4.2 mm of water applied was sufficient to replace evaporation loss and return the surface soil to field capacity. The fumigated area was divided into 3 blocks. Treatments were tested with three replicates in a randomized complete block design. A 3-m-wide buffer zone was left between blocks and treatments with and without water applications.

Sampling and Measurement

Sampling for air emissions and distribution of applied fumigants in the soil gas phase was continued for 9 d. Soil samples were taken at the end of the sampling period for residual fumigants in the soil. Soil water content was determined for the control and water application plots on the first day of fumigation and at the end of the field trial. Soil temperature at 10-cm depth was measured during the last day of the trial.

Emission samples were collected using closed, passive (open bottom) gas chambers assembled from inverted Leaktite galvanized steel buckets (Leaktite Co., Leominster, MA). The dimension of the emission chambers were 18.6 (top i.d.) \times 15.0 (height) \times 20.7 cm (bottom i.d.). The volume of the chamber and the surface area it covers were 4.6 L and 337 cm^2 , respectively. At the top center of the chamber, a sampling port with a Teflon-faced silicone rubber septum (3 mm thick, Supelco, Bellefonte, PA) was installed for withdrawing gas samples. For treatments with plastic tarps, the chamber was sealed to the plastic film with silicone rubber sealant. Our preliminary tests showed that there was no interference of the sealant with the analysis of the fumigants, i.e., compounds volatilized from the sealant and captured in the chamber had substantially different retention time in gas chromatography columns in comparison with 1,3-D and CP. For treatments with no plastic tarp, the chamber bottom was pushed a few centimeters into the soil, depending on the hardness of the soil. For example, when surface water was applied after fumigation, a surface crust formed that did not allow the chamber to be pushed into the soil more than 1 cm deep. In this case, after good contact between the chamber and the soil was created, the chamber edge was covered with more surrounding soil.

Table 1. Selected properties of Hanford sandy loam soil.

Measurements	Values
Bulk density, g cm^{-3}	1.55 (range 1.45–1.65)
Sand, g kg^{-1}	548
Silt, g kg^{-1}	396
Clay, g kg^{-1}	56
Water content at 33 kPa suction, $\text{g kg}^{-1}\dagger$	170
Water content at 1500 kPa suction, $\text{g kg}^{-1}\dagger$	54
pH (1:1 soil/water extract)	7.2
EC (1:1 soil/water extract), dS m^{-1}	0.31
CEC, $\text{cmol}_\text{c} \text{ kg}^{-1}$	6.8
Organic matter content, g kg^{-1}	7.2

\dagger Source: Skaggs et al. (2004).

The gas sampling chambers were placed on soil or tarp for 30 min. At the end of the 30-min period, a 120-mL gas sample from inside the chamber was withdrawn using a gas-tight syringe through the sampling port and through an ORBO 613, XAD-4 80/40mg (Supelco, Bellefonte, PA) tube for trapping both 1,3-D and CP. We determined in preliminary tests that the XAD resin could trap 1,3-D as efficiently as CP ($95 \pm 6\%$) under the sampling conditions, i.e., flow rate $\sim 100 \text{ mL min}^{-1}$. The sampling tubes were immediately capped at both ends, stored on dry ice in the field and in a freezer (-18°C) in the laboratory, and extracted within 6 wk for fumigant analysis using the procedures described below. Thirty minutes was chosen for chamber capture time to accumulate fumigant concentrations within the chamber high enough to be detected throughout the field trial period. One gas sampling chamber was used for each plot. Samples were collected every 2 to 3 h for the first 48 h and every 4 h thereafter during the day. No sampling was done at night (2100 to 0600 h for the first two nights and 1700 to 0800 h thereafter). For water application treatments, sampling was conducted before and after each water application. Field blank samples were taken at about 500 m away from the field site during the trial.

The passive or closed chamber method allows direct measurement of gas volatilization from soil to the atmosphere (Yates et al., 2003). Upon placing the chamber over the soil surface, the concentration of fumigants in the chamber increases with time as the chemical moves from the soil matrix into the chamber. The concentrations of 1,3-D and CP within the chamber at the end of the 30 min. capture time were determined. Based on the fumigant concentration within the chamber, capture time, chamber volume, and surface area, the average emission rate (flux) during the capture time was calculated and compared among treatments. Because diffusion rate of the fumigants into the chamber is expected to decrease as a function of time (due to concentration gradient decreases), the average emission rate measured was likely lower than the initial rate (representative of the rate without the chamber). Thus, average emission rates obtained likely underestimate actual emission rates (Yates et al., 2003). Cumulative emissions of 1,3-D and CP were estimated by summing the products of the average of two consecutive emission flux values and the time interval between the two measurements over the time span of the study.

Probes for sampling fumigants in the soil-gas phase were installed in one replicate of the treatments following fumigation and surface treatments. These probes were stainless steel tubing with 0.1-mm i.d. inserted with the lower ends at depths of 10, 30, 50, 70, and 90 cm below the soil surface. A 50-mL soil gas sample was withdrawn through an ORBO 613, XAD 4 80/40mg tube using a custom-made sampling apparatus. Soil gas samples were collected at 6, 12, 24, 30, 36, 48, 72, 120, 168, and 216 h following fumigation. Processing of the sampling tubes was the same as the emission samples.

For residual fumigants in the soil, soil samples were taken at the end of the field trial at 20-cm depth intervals to 100 cm. Samples were collected with an auger (7 cm i.d.), mixed, and placed in a screw-top glass jar on dry ice in the field, and stored in a freezer (-18°C) in the laboratory until analyzed.

Sample Extraction and Analysis

The XAD sampling tubes were broken in the middle and all materials in the tube were transferred into a 10-mL clear crimp-top vial. Five mL of hexane was added to the vial and after crimp sealed the vials were shaken for 2 h on a reciprocating shaker at 120 strokes min^{-1} . After settling, a portion of the extract was transferred to a 2-mL amber GC vial and

the vials were stored for no more than 4 wk in a freezer (-18°C) until analysis. Our test showed that 95% of the fumigant was recovered in the solvent after storing in the freezer for 4 wk.

The 1,3-D and CP in the extracts were analyzed using a GC- μECD (Agilent Technology 6890N Network GC system with a micro electron capture detector [μECD]; Agilent Technology, Palo Alto, CA). A DB-VRX capillary column (30-m length \times 0.25 mm i.d. \times 1.4 μm film thickness, Agilent Technologies, Palo Alto, CA) was used for separation of fumigants. The GC carrier gas (He) flow rate, inlet temperature, and detector temperature were set at 2.0 mL min^{-1} , 150, and 300°C , respectively. The oven temperature program was as follows: initially 45°C , increasing at $2.5^\circ\text{C min}^{-1}$ to 75°C , then at $99^\circ\text{C min}^{-1}$ to 110°C and held for 7 min. The retention time for cis-1,3-D, trans-1,3-D, and CP were 8.6, 9.6, and 10.7 min, respectively. The detection limits (three times the standard deviation of the background noise level) of our methods were 0.01, 0.01, and 0.001 mg L^{-1} for cis-1,3-D, trans-1,3-D, and CP, respectively, when an injection volume of 1- μL solution was used. The total 1,3-D emissions, soil gas concentrations, and residual concentrations in soils reported in the results are the sum of cis- and trans-1,3-D.

Soil sample extractions followed the procedures from Guo et al. (2003). Before defrosting, 8 g equivalent dry weight of soil was weighed into a 21-mL crimp-top extraction vial. Eight mL of ethyl acetate was added to the vial that contained various amounts of Na_2SO_4 to adsorb soil moisture (at a 7:1 ratio of Na_2SO_4 /water depending on the soil water content). The vial was crimp-sealed with aluminum caps and Teflon-faced butyl-rubber septum, mixed, and incubated at 80°C in a water bath overnight ($\sim 18 \text{ h}$). This method extracts more than 95% of the fumigant in soils. After settling, a portion of the supernatant was transferred into a 2-mL amber GC vial for fumigant analysis using the GC- μECD as described above, except using ethyl acetate as the standard and sample solvent. The vials were stored in a freezer (-18°C) for no more than 4 wk before analysis.

Statistics

For statistical analysis, SAS Version 9.1 (Littell et al., 2002) was used. Data were analyzed with the two-way factorial analysis of variance (ANOVA) and means were separated using Tukey's HSD (honestly significant difference) test.

RESULTS AND DISCUSSION

Emission Reductions

Emission Flux

Emission fluxes for 1,3-D and CP from various treatments are shown in Fig. 1 and 2, respectively. All blanks taken away from the field showed nondetectable fumigants indicating no interference from the surrounding area during the field trial. Measurement of emissions started 2 h after fumigation. For both the control and HDPE-tarp-dry soil treatments, 1,3-D emission rate rapidly increased within the first 12 h (up to $40 \mu\text{g m}^{-2} \text{ s}^{-1}$) and reached maximum measured peak emission by 24 h. The peak emission rate for the control likely occurred during the first night when no samples were collected (indicated by the dashed line in Fig. 1 and 2) and likely exceeded $80 \mu\text{g m}^{-2} \text{ s}^{-1}$ for 1,3-D. The peak emission rate for the HDPE tarp over dry soil

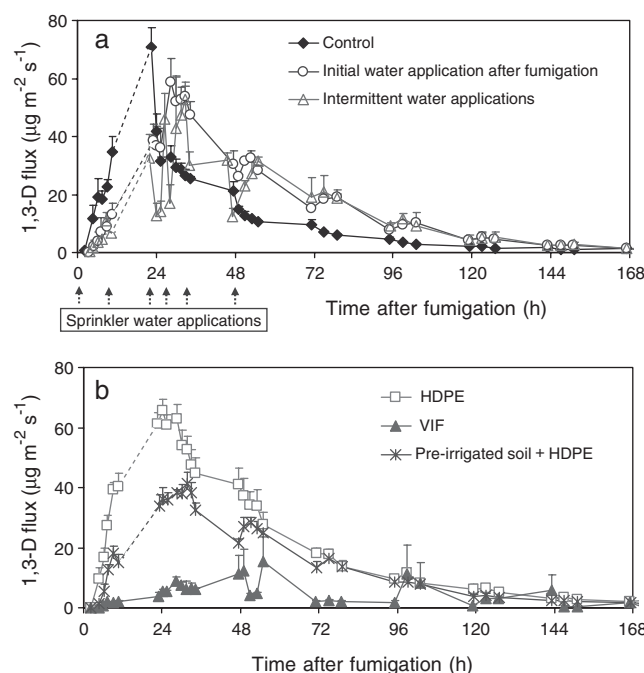


Fig. 1. Effects of surface seal treatment ([a] water seals; [b] plastic tarps) on emission flux of 1,3-dichloropropene (1,3-D) after shank injection of Telone C35 in a field trial. Error bars are the standard error of the mean ($n = 3$). Dashed lines indicate uncertainty when no measurements were made. HDPE, high density polyethylene; VIF, virtually impermeable film.

likely occurred early the second morning (about 22 h after fumigation).

The initial water application immediately after fumigation delayed fumigant emissions for at least 2 to 3 h. The flux at 12 h for this treatment was below $14 \mu\text{g m}^{-2} \text{s}^{-1}$ (Fig. 1a) and the peak flux did not occur until 30 h. The reduced emission rates from initial water application within the first 12 h after fumigation can be important to protect workers and bystanders immediately after fumigation. Each intermittent water application resulted in an abrupt reduction in emission rates (to less than $20 \mu\text{g m}^{-2} \text{s}^{-1}$ for 1,3-D and $2 \mu\text{g m}^{-2} \text{s}^{-1}$ for CP), although the emission rates rebounded quickly within 3 to 4 h. The results were similar to previous column tests with this soil (Gao and Trout, 2006) in which water seals dramatically reduced emissions but only temporarily. The abrupt emissions reduction indicates this could be a very effective way to quickly reduce emissions if excessive air concentrations are detected.

The HDPE tarp over the pre-irrigated soil resulted in a flatter emission curve (Fig. 1b) and generally lower emission rate peak ($40 \mu\text{g m}^{-2} \text{s}^{-1}$ for 1,3-D) than the control or HDPE tarp alone ($66 \mu\text{g m}^{-2} \text{s}^{-1}$). The VIF tarp showed the lowest emission rates with most values below $10 \mu\text{g m}^{-2} \text{s}^{-1}$ for 1,3-D (Fig. 1b) and $3 \mu\text{g m}^{-2} \text{s}^{-1}$ for CP (Fig. 2b). Variations of emission rates among VIF tarp replicates were observed especially after 2 d and may represent nonuniform permeability of the VIF.

The emission fluxes of CP (Fig. 2) followed similar patterns as 1,3-D but the emission rates were lower. The amount of CP applied was about 57% of 1,3-D on a

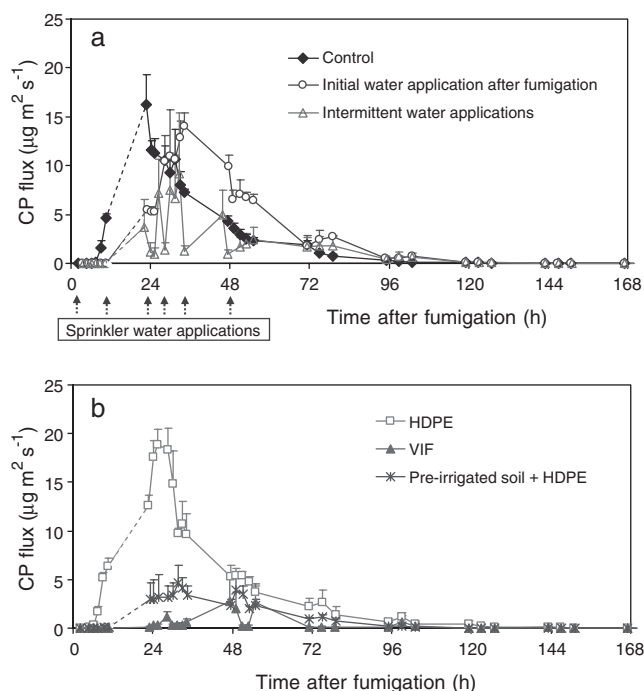


Fig. 2. Effects of surface seal treatment ([a] water seals; [b] plastic tarps) on emission flux of chloropicrin (CP) after shank injection of Telone C35 in a field trial. Error bars are the standard error of the mean ($n = 3$). Dashed lines indicate uncertainty when no measurements were made. HDPE, high density polyethylene; VIF, virtually impermeable film.

weight basis. The emission rates for CP were all below $20 \mu\text{g m}^{-2} \text{s}^{-1}$ for both the control (Fig. 2a) and HDPE tarp treatments (Fig. 2b), with peak values less than 25% of the 1,3-D fluxes. At the end of the monitoring period, CP emissions in most plots were nondetectable.

Cumulative Emissions

Cumulative emission losses of 1,3-D and CP are shown in Fig. 3 and summarized in Table 2. Emission rate data indicated that the peak emissions for the control treatment were likely missed during the first night. Previous column studies had shown that higher emission peaks and earlier peak times were expected for the control than with tarp (e.g., Gan et al., 1998; Gao and Trout, 2006). These studies also indicated that the peak emission rate for the control was about 1.5 times of that from HDPE tarp. By assuming this peak value was reached during the first night for the control, the total cumulative emission could increase 25% from the estimated value in Table 2. The modified total emission loss, however, is still substantially lower than the total emission loss from HDPE tarp. We highly suspect that the passive chamber method might underestimate fumigant emissions from a bare and dry soil surface because a perfect seal between the chamber and the soil was difficult to form during the 30 min capture time. Thus, cumulative emission for the control was believed to be substantially underestimated as evidenced by its lower total emissions estimated from measurements than several surface

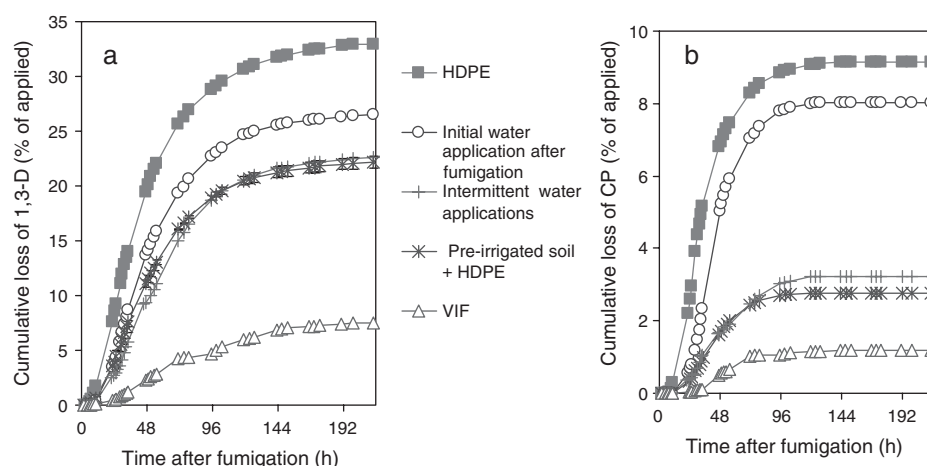


Fig. 3. Comparison of surface seal treatments on cumulative emissions of (a) 1,3-dichloropropene (1,3-D) and (b) chloropicrin (CP) after shank injection of Telone C35 in a field trial. HDPE, high density polyethylene; VIF, virtually impermeable film.

seal treatments (Table 2). For other treatments, the peak emissions were observed at or after 22 h of fumigation and the estimated total emission losses in Table 2 would increase about 3 to 8% by assuming the high emission rates observed early on the second morning occurred earlier. For this reason, our discussion below focuses on comparisons between surface seal treatments.

Cumulative emission losses of 1,3-D and CP are shown in Fig. 3 as a percentage of fumigant applied. Note that the emission measurement process was designed to measure relative emissions among treatments rather than to conduct a total mass balance. Estimates of total emission losses for the 9-d monitoring period are shown in Table 2. The total 1,3-D emission loss was 33, 27, 24, 22, and 8% of applied for the HDPE tarp only, initial water application immediately following fumigation, intermittent water applications following fumigation, pre-irrigated soil plus HDPE tarp, and VIF tarp, respectively. The total emission loss of CP for these treatments was smaller but followed the same

trend (i.e., 9, 8, 4, 3, and 1% of applied for these treatments, respectively). The actual total emissions are likely higher than these values because average emission rates over a 30-min period were used to estimate the total emission loss and the diffusion rates into the emission chamber are expected to decrease as concentration in the chamber increases with time (Yates et al., 2003). The generally lower emissions of total applied for CP than 1,3-D were due to the different properties of the two chemicals and may be partially due to their different application rates. The CP has lower solubility (2.0) than 1,3-D (2.2) and much lower vapor pressure (24 kPa or 18 mm Hg) than 1,3-D (45 kPa or 34 mm Hg) (Ajwa et al., 2003) indicating less volatility of CP than 1,3-D. Chloropicrin also has much shorter aerobic soil metabolism half-life than 1,3-D. For a sandy loam soil, the half-life of 1,3-D was 6.3 d (Dungan et al., 2001) compared with 1.5 d for CP (Gan et al., 2000) at 20°C.

The HDPE tarp was the poorest and VIF was the most effective barrier to 1,3-D and CP among the surface seal treatments. Pre-irrigated soil plus HDPE tarp and the intermittent water applications were relatively effective methods to reduce total emissions. The continuous evaporation and condensation of water under the plastic film may form an effective moisture barrier to fumigants at the soil surface. The single sprinkler water application following fumigation reduced total emissions, but not significantly different from the HDPE tarp over dry soil. The water seal may be more effective to reduce CP than 1,3-D emissions based on data in Fig. 3 and due to its shorter half-life.

Our estimate of total emissions based on measurements for the control was lower than the HDPE tarp based on measured emissions (Table 2) and the reasons for this underestimate were discussed above. Tests on emissions from column experiments at room temperature (~22°C) using the same soil showed that the emission peak of 1,3-D under HDPE tarp was 87% of the dry, nontarped control with a delayed peak time of 1 to 2 h (Gao and Trout, 2006). Gan et al. (1998) also showed that the peak volatilization rates of 1,3-D from

Table 2. Cumulative emission loss of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) for surface seal treatments measured over 9 d after fumigation.†

Treatment	Total loss‡		Total loss§	
	1,3-D	CP	1,3-D	CP
	— g m ⁻² —		— % applied —	
Control¶	7.40b	1.48b	19.8 (1.8)	7.0 (0.8)
HDPE	12.27a	1.95a	33.0 (4.1)	9.2 (2.1)
VIF	2.79c	0.25c	7.5 (3.7)	1.2 (0.8)
Pre-irrigated soil plus HDPE	8.23b	0.59bc	22.1 (0.9)	2.8 (1.2)
Initial water application	9.85ab	1.71ab	26.5 (2.5)	8.0 (4.1)
Intermittent water applications	9.00b	0.81bc	24.2 (6.2)	3.2 (2.8)

† HDPE, high density polyethylene; VIF, virtually impermeable film; 1,3-D, 1,3-dichloropropene; CP, chloropicrin.

‡ Within a column, means ($n = 3$) with the same letter are not significantly different ($\alpha = 0.05$).

§ Values in parenthesis are standard deviations of the mean ($n = 3$).

¶ The low emission loss from the control was believed to be underestimated due to no measurements made during the first night after fumigation when emissions were high (see Fig. 1), and possible poor sealing between the passive chamber and a dry surface soil during measurement. Use of these values needs precaution. We expect emission loss from the control should not be lower than that from HDPE tarp.

soil columns after injection at 20 cm was higher for nontarped control ($\sim 1100 \mu\text{g h}^{-1}$) than the HDPE tarped treatment ($\sim 750 \mu\text{g h}^{-1}$) with a few hours earlier peak time. Their results showed that total emission loss of 1,3-D was 64% of applied in the control compared with 58% in HDPE tarped treatment. We conducted a further field trial on the same soil and measured emission rate differences between the nontarped control and HDPE tarped treatment by continuously sampling the air just above the soil surface. Results (not shown) clearly showed initially higher fumigant concentrations

and earlier peak time above nontarped soil surface than HDPE tarp.

Fumigants in Soil Gas Phase

Distribution of 1,3-D and CP in the soil gas phase is shown in Fig. 4 and 5, respectively. Similar patterns were observed between the two fumigants except that concentrations of CP were lower than 1,3-D. The differences in the concentration range and peaks between CP (maximum 25 mg L^{-1}) and 1,3-D (maximum 33 mg L^{-1}) were greater than their application ratio ($\text{CP}/1,3\text{-D} = 1:1.7$;

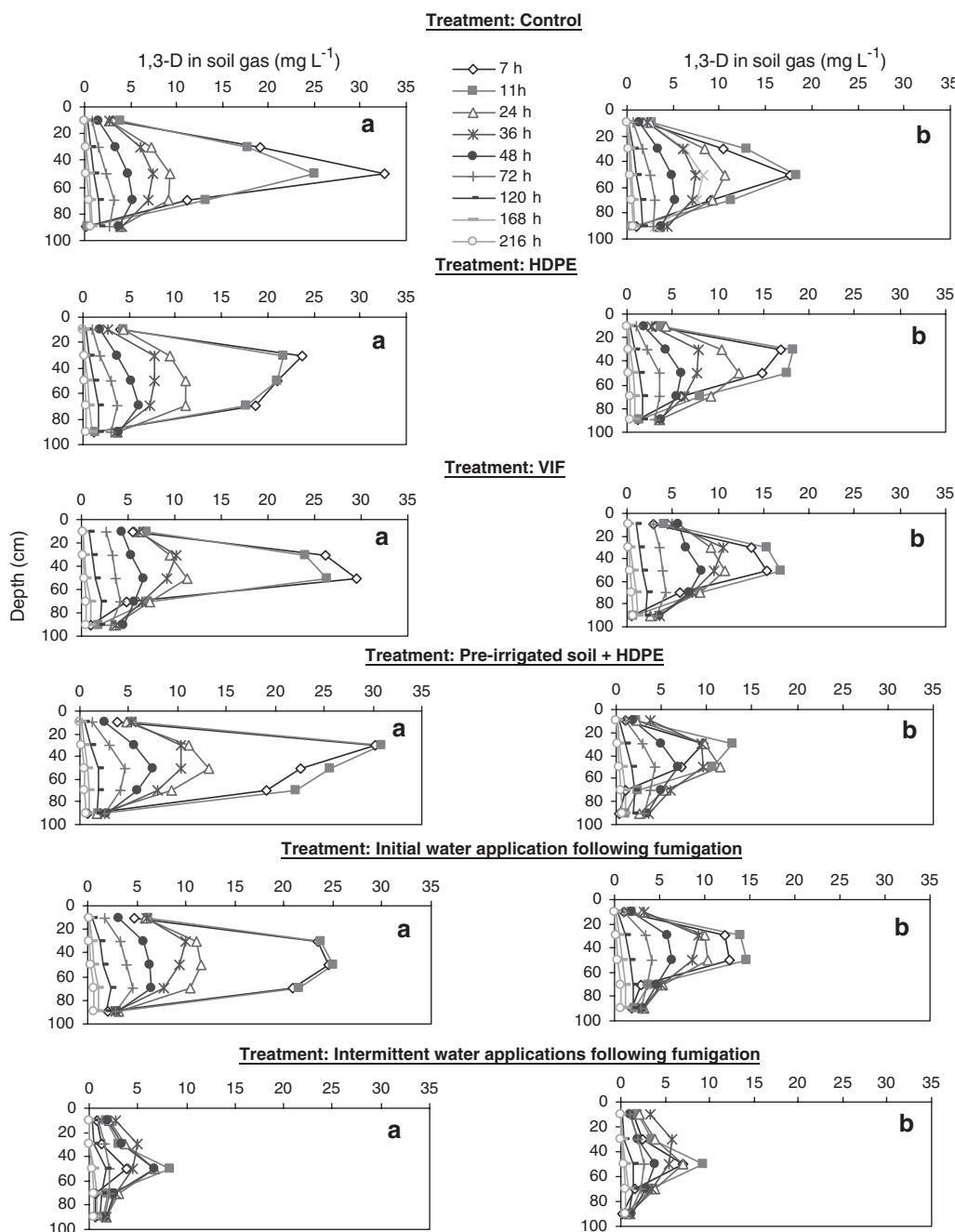


Fig. 4. Distribution of 1,3-dichloropropene (1,3-D) in soil gas phase after shank injection of Telone C35 under various surface treatments. Sampling was located (a) adjacent to fumigant injection line, or (b) between injection lines. HDPE, high density polyethylene; VIF, virtually impermeable film.

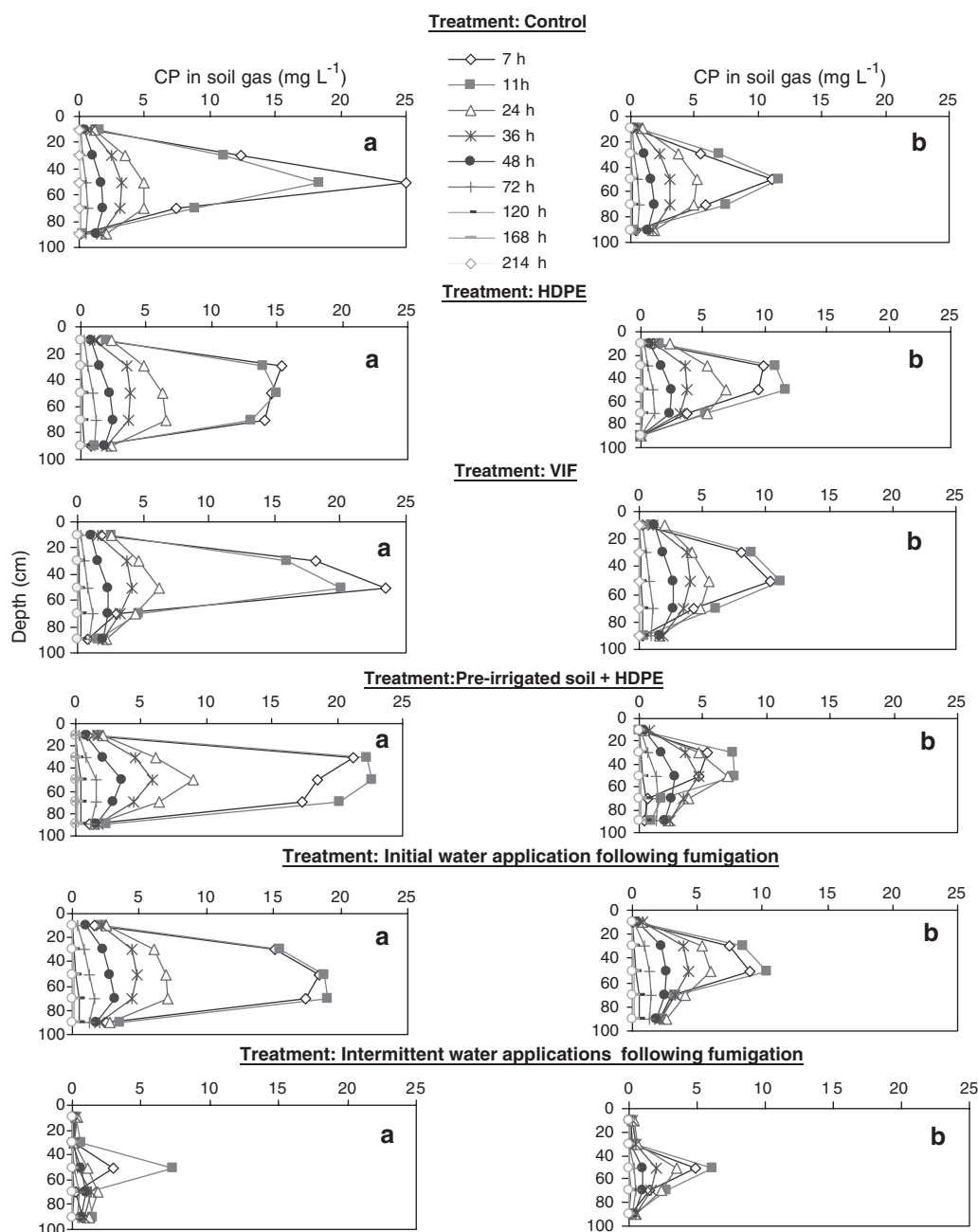


Fig. 5. Chloropicrin (CP) distribution in soil gas phase after shank injection of Telone C35 under various surface treatments. Sampling was located (a) adjacent to fumigant injection line, or (b) between injection lines. HDPE, high density polyethylene; VIF, virtually impermeable film.

i.e., higher portion of CP was measured in soil gas compared with 1,3-D). Recall that relative CP emissions were less than the application ratio. These results indicated that CP remained in the soil proportionally higher initially than 1,3-D. By the end of the field trial, however, CP dissipated from the soil to very low levels ($<0.1 \text{ mg L}^{-1}$) in most treatments compared with 1,3-D concentrations that were up to 0.6 mg L^{-1} . This was due to the lesser amount of CP applied as well as its more rapid degradation rate than 1,3-D.

A difference in fumigant distribution was observed between sampling locations, i.e., adjacent to fumigant injection lines (Fig. 4a and 5a) and between injection

lines (Fig. 4b and 5b) during the first 24 h. The highest concentrations were observed within 12 h near injection lines compared with about 50% lower peak concentrations between injection lines. This initial nonuniform fumigant concentration when Telone C35 was shank-applied with a spacing of 46 cm indicates that 24 h is required to laterally distribute the fumigants.

Measured concentrations of both 1,3-D and CP in the soil gas phase were much lower with intermittent water application compared with other treatments. This was not observed in our previous column experiments when 13 mm water was applied intermittently to soil surface (Gao and Trout, 2006). Although the total amount of

water applied in the field trial was 40 mm, we cannot conclude that the amount of water applied resulted in the lower fumigant concentrations in the field trial. The intermittent water application treatment included the initial water application immediately following fumigation and was followed by the second water application 8 h after fumigation. Before 8 h, measured fumigant concentrations in the intermittent water application plot were substantially lower than in the initial water application plot. The reason for the lower measured fumigant concentration in the intermittent water application could not be determined but may be due to soil variability (note that soil gas samples were not replicated). Nonetheless, it should be noted that as soil water content increases, the diffusion of fumigants in soils generally decreases. Excessive water could limit the diffusion of fumigants in the soil and reduce fumigation efficacy. Thomas et al. (2003) observed in a sandy soil that fumigant diffusion was negligible in near-water-saturated soil and fumigant diffusion in near-field capacity soil was between the rates of dry soil and near-saturated soil. For fine-textured soils, the effect of water content on fumigant diffusion was most striking when soils had water contents in excess of 50 kPa moisture tension at 30-cm depth (McKenry and Thomason, 1974). Thus, an optimum soil water content is needed to prevent rapid emissions while maintaining adequate pest control.

The ability of VIF tarp to retain higher 1,3-D concentrations in the soil gas was relatively less in this field trial than was observed in the previous column tests. Although significantly higher fumigant concentrations under the VIF tarp than other treatments were observed during early intermediate time periods (e.g., 36 and 48 h), there were no significant differences in fumigant concentrations under VIF tarp compared with other treatments at the end of the measurement period. The soil was cultivated to about 76-cm depth before fumigation and downward movement of fumigant below the lowest sampling depth is indicated by the fumigant concentrations measured at the 90-cm depth at 36 and 48 h (Fig. 4 and 5). The lower than expected fumigant concentrations under VIF may indicate lateral movement because the VIF tarp used was only 3 m wide and fumigants may have degraded significantly in the soil over 9 d. Others have found that VIF maintained high fumigant concentrations under the tarp, which can improve and may allow lower fumigation rates (Noling, 2002b; Gilreath et al., 2005; Santos et al., 2005).

Residual Fumigant in Soil

Residual fumigants in the soil (solid and liquid phase combined) were extracted from soil samples taken at the end of the field trial and the results for 1,3-D are shown in Fig. 6. Nondetectable or extremely low CP concentrations ($<0.01 \text{ mg kg}^{-1}$) were measured. This indicates that CP had degraded in the soils within 9 d, as was corroborated by the soil gas data. For 1,3-D, detectable concentrations were found in soils in the upper 40 cm in most treatments and to 60 cm for the VIF. Concentrations of 1,3-D were relatively higher in shallow soil

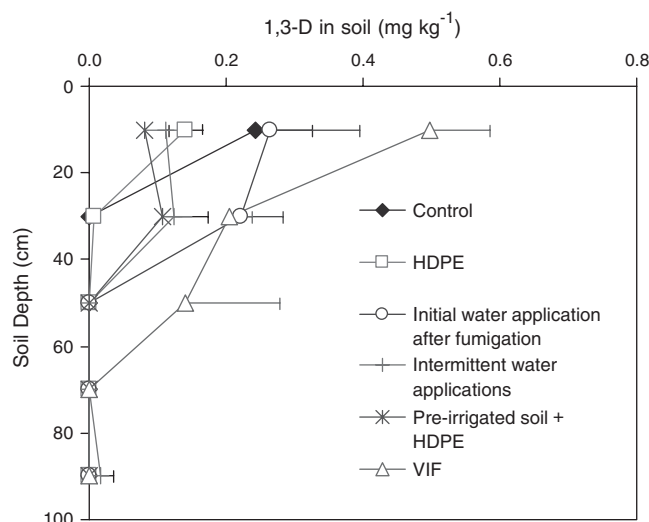


Fig. 6. 1,3-dichloropropene (1,3-D) extracted from soil samples collected 9 d after field applications of Telone C35. Horizontal bars are the standard error of the mean ($n = 3$). HDPE, high density polyethylene; VIF, virtually impermeable film.

layers for all the treatments. The highest 1,3-D concentrations (average 0.5 mg kg^{-1}) were observed under the VIF tarp (significantly higher than all other treatments at $\alpha = 0.05$). There were no significant differences between other treatments.

Soil Water Content

Soil water content varied as a result of the irrigation events. On the first day of fumigation, pre-irrigated soil from 3- to 15-cm depth had a water content of 138 g kg^{-1} (13.8%) (2 d after sprinkling 56 mm water) and soil from the initial water application (19 mm) from 2- to 6-cm depth had a water content of 132 g kg^{-1} (a few hours after application). These results indicate that the surface soil was holding water at below its field capacity (170 g kg^{-1}) a few hours after application. Sufficient and/or frequent water applications may be needed to keep the soil surface at a high water content to reduce emissions. This supports the emission data that water application to the soil surface reduced fumigant emissions immediately following each water application; however, the emission rate rebounded quickly and approached those without water application within a few hours (Fig. 1a and 2a). At the end of the field trial, water content in surface soils (0- to 20-cm depth) decreased to 40 to 60 g kg^{-1} from the water application treatment plots due to evaporation and downward redistribution. Soil bulk density, however, was not affected by the water application based on the data obtained from plots for the control and the intermittent water application treatment (data not shown).

Soil Temperature

Tarpping and water application have large effects on soil temperature. The maximum soil temperature mea-

Table 3. The maximum soil surface temperature measured during the last day of the field trial.

Treatment†	Maximum temperature (°C)‡
Control	36.1d
HDPE	44.5b
VIF	43.6b
Pre-irrigated soil plus HDPE	46.6a
Initial water application	39.1c
Intermittent water applications	38.0c

† HDPE, high density polyethylene; VIF, virtually impermeable film.

‡ Within a column, means ($n = 3$) with the same letter are not significantly different ($\alpha = 0.05$).

sured 10 cm below the soil surface during the last day of the field trial is shown in Table 3. Pre-irrigated soil plus HDPE tarp resulted in the highest temperature (47°C) among the treatments followed by the dry soil with either HDPE or VIF tarp. Higher temperatures would result in a higher Henry's law constant and diffusion rate, a higher permeability of tarps, and a lower solubility of fumigants. As a result, tarping may not help reduce emissions. The high temperature may also result in a benefit for controlling soil pests from the solarization effects as reported by others (e.g., Minagawa et al., 2004; Sharma et al., 2004). Thus, tarping over a moist soil may improve the overall soil pest control at high temperature conditions and at the same time, reduce 1,3-D emissions. However, tarps are an expensive alternative compared with water seals alone.

CONCLUSIONS

This research confirmed that water applications to the soil surface following fumigation can reduce 1,3-D and CP emissions from shank application of Telone C35 more effectively than standard HDPE tarp on dry soil. However, several intermittent water applications over 48 h were required to maintain sufficiently high surface soil water content in the tested sandy loam soil to significantly reduce emissions. The pre-irrigated soil plus HDPE tarp treatment reduced emissions similarly to the intermittent water applications. This treatment also resulted in the highest soil surface temperature, which may improve broad-spectrum pest control from solarization effects in the surface soil. The benefit of initial water application immediately after fumigation would be the delay of emission peak time and concentration, which would reduce the risks to workers and bystanders following fumigation. The VIF tarp was by far the most effective method tested that reduced fumigant emissions as well as maintained high fumigant concentrations in the soils. Large field trials are needed to evaluate emissions and test application practices associated with VIF tarping.

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REFERENCES

- Ajwa, H.A., S. Klose, S.D. Neilson, A. Minuto, M.L. Gullino, F. Lamberti, and J.M. Lopez-Aranda. 2003. Alternatives to methyl bromide in strawberry production in the United States of America and the Mediterranean Region. *Phytopathol. Mediterr.* 42:220–244.
- California Department of Pesticide Regulation. 2003. Pesticide use report data. California Department of Pesticide Regulation, Sacramento, CA.
- Casanova, J.L. 2002. An overview of the scientific aspects of ozone depletion and their impact on the environment. p. 23–27. *In* Proc. Int. Conf. Alt. MeBr "The Remaining Challenges". Sevilla, Spain, 5–8 Mar. 2002. European Communities, Belgium.
- Dungan, R.S., J. Gan, and S.R. Yates. 2001. Effect of temperature, organic amendment rate, and moisture content on the degradation of 1,3-dichloropropene in soil. *Pest Manage. Sci.* 57:1107–1113.
- Gao, S., and T. Trout. 2006. Surface water applications reduce 1,3-dichloropropene emissions from soil fumigation. *J. Environ. Qual.* 35:1040–1048.
- Gan, J., S.R. Yates, F.F. Ernst, and W.A. Jury. 2000. Degradation and volatilization of the fumigant chloropicrin after soil treatment. *J. Environ. Qual.* 29:1391–1397.
- Gan, J., S.R. Yates, D. Wang, and F.F. Ernst. 1998. Effect of application methods on 1,3-D volatilization from soil under controlled conditions. *J. Environ. Qual.* 27:432–438.
- Gilreath, J.P., T.N. Motis, and B.M. Santos. 2005. *Cyperus* spp. control with reduced methyl bromide plus chloropicrin rates under virtually impermeable films in pepper. *Crop Prot.* 24:285–287.
- Guo, M., S.K. Papiernik, W. Zheng, and S.R. Yates. 2003. Formation and extraction of persistent fumigant residues in soils. *Environ. Sci. Technol.* 37:1844–1849.
- Honaganahalli, P.S., and J.N. Seiber. 1997. Health and environmental concerns over the use of fumigants in agriculture: The case of methyl bromide. p. 1–13. *In* J.N. Seiber et al. (ed.) *Fumigants: Environmental fate, exposure, and analysis*. ACS Symposium Series 652. ACS, Washington, DC.
- Jin, Y., and W.A. Jury. 1995. Methyl bromide diffusion and emission through soil columns under various management techniques. *J. Environ. Qual.* 24:1002–1009.
- Littell, R.C., W.W. Stroup, and R.J. Freund. 2002. SAS for linear models. 4th ed. SAS Institute, Cary, NC.
- McKenry, M.V., and I.J. Thomason. 1974. 1,3-dichloropropene and 1,2-dibromoethane Compounds: I. Movement and fate as affected by various conditions in several soils. *Hilgardia* 42(11):383–421.
- Minagawa, N., S. Aiba, K. Katayama, and K. Miura. 2004. Effect of field solarization on control of soil nematodes. *Bull. Nat. Agric. Res. Center.* 2004(4):25–34.
- Noling, J.W. 2002a. Reducing methyl bromide field application rates with plastic mulch technology. Publication ENY-046, Institute of Food and Agricultural Sciences, University of Florida, Gainesville, FL. Available at <http://edis.ifas.ufl.edu/IN403> (accessed 14 Mar. 2006; verified 28 Aug. 2006).
- Noling, J.W. 2002b. The practical realities of alternatives to methyl bromide: Concluding remarks. *Phytopathology* 92:1373–1375.
- Papiernik, S.K., and S.R. Yates. 2002. Effect of environmental conditions on the permeability of high density polyethylene film to fumigant vapors. *Environ. Sci. Technol.* 36:1833–1838.
- Santos, B.M., J.P. Gilreath, and T.N. Motis. 2005. Managing nutsedge and stunt nematode in pepper with reduced methyl bromide plus chloropicrin rates under virtually impermeable films. *HortTechnol.* 15:6–9.
- Segawa, R. 2005. Volatile organic compound (VOC) emissions from pesticides. California Department of Pesticide Regulation, Sacramento, CA. Available at <http://www.cdpr.ca.gov/docs/pur/vocproj/vocmenu.htm> (accessed 14 Mar. 2006; verified 28 Aug. 2006).
- Sharma, S.K., V.S. Verma, A. Sharma, and M. Gupta. 2004. Effect of soil solarization on soil microflora with special reference to *Fusarium solani* in mango nurseries. *Plant Dis. Res. Ludhiana.* 19(2): 144–150.

- Skaggs, T.H., T.J. Trout, J. Simunek, and P.J. Shouse. 2004. Comparison of HYDRUS-2D simulations of drip irrigation with experimental observations. *J. Irrig. Drain. Eng.* 130:304–310.
- Sullivan, D.A., M.T. Holdsworth, and D.J. Hlinka. 2004. Control of off-gassing rates of methyl isothiocyanate from the application of metam-sodium by chemigation and shank injection. *Atmos. Environ.* 38:2457–2470.
- Thomas, J.E., L.H. Allen, Jr., L.A. McCormack, J.C. Vu, D.W. Dickson, and L.T. Ou. 2003. Diffusion and emission of 1,3-dichloropropene in Florida sandy soil in microplots affected by soil moisture, organic matter, and plastic film. *Pest Manage. Sci.* 60:390–398.
- Thomas, J.E., L.H. Allen, Jr., L.A. McCormack, J.C. Vu, D.W. Dickson, and L.T. Ou. 2004. Atmospheric volatilization and distribution of (Z)- and (E)-1,3-dichloropropene in field beds with and without plastic covers. *J. Environ. Sci. Health B* 39:709–723.
- Thomas, J.E., L.T. Ou, L.H. Allen, Jr., L.A. McCormack, J.C. Vu, and D.W. Dickson. 2006. Henry's law constants and mass transfer coefficients for methyl bromide and 1,3-dichloropropene applied to Florida sandy field soil. *Chemosphere* 62:980–988.
- Trout, T. 2005. Fumigant use in California. p. 12(1–5). In *Proc. Ann. Int. Res. Conf. on MeBr Alternatives and Emission Reductions*. San Diego, CA, 31 Oct.–3 Nov. 2005. Available at <http://www.mbao.org/2005/05Proceedings/mbrpro05.html> (accessed 14 Mar. 2006; verified 28 Aug. 2006).
- Wang, D., S.R. Yates, F.F. Ernst, J. Gan, F. Gao, and J.O. Becker. 1997. Methyl bromide emission reduction with field management practices. *Environ. Sci. Technol.* 31:3017–3022.
- Wang, D., S.R. Yates, J. Gan, and J.A. Knuteson. 1999. Atmospheric volatilization of methyl bromide, 1,3-dichloropropene, and propargyl bromide through two plastic films: Transfer coefficient and temperature effect. *Atmos. Environ.* 33:401–407.
- Yates, S.R., J. Gan, and S.K. Papiernik. 2003. Environmental fate of methyl bromide as a soil fumigant. *Rev. Environ. Contam. Toxicol.* 177:45–122.